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POLYNUCLEAR COMPLEXES OF FIRST-ROW TRANSITION METAL IONS

Submitted by

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Introduction

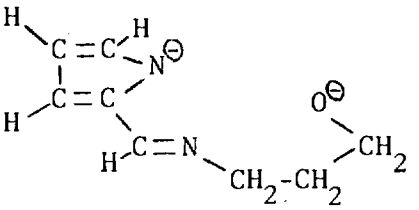
Considerable progress has been made during the year on the problems outlined in the proposal. In the area of oxygen-bridged complexes, structures were determined for copper(II) compounds with planar and bent four-membered rings and structures were determined for a series of iron(III) complexes. Studies of hydrogen-bonded dimers were continued and structure studies were completed for complexes of nickel(II) and copper(II) with a tetradentate diimine ligand; a structure study of an additional hydrogen-bonded dimer of nickel(II), in which there are three O-H-O bonds, has also been completed. Investigations of complexes with other bridging groups were initiated and a structure study of an oxime-bridged copper(II) complex has been completed. These studies are described briefly in the following paragraphs. In the course of our work on polynuclear complexes, several interesting mononuclear complexes have been investigated and results of those studies are also summarized in this report.

Oxygen-Bridged Copper(II) Complexes

A compound with the formula $[Cu(O\text{-}(CH_2)_3\text{-}NH_2)(C_2H_3O_2)]_2$ was prepared and its structure was determined by x-ray diffraction. The structure consists of square-planar copper(II) complexes bridged into dimers by the alkoxide groups. The aminoalkoxide is chelated and the acetate functions as a monodentate ligand. The four-membered copper-oxygen ring is planar and the magnetic moment is low, 0.40 B.M. at room temperature.

The crystal structure of the compound $CuL\cdot 2H_2O$ (where L represents the dianion of the amide, I, formed by the condensation of picolinic acid and

3-aminopropanol) has been studied by x-ray diffraction. Final residual



I

factors for the 1279 reflections above 3σ are R = 0.043 and R_w = 0.031. The structure, Figure 1, consists of dimeric units, $[CuL(H_2O)]_2$, and waters of crystallization that are linked by weak hydrogen bonding into an infinite nearly-planar network. The dimeric unit has two-fold symmetry and contains a bent Cu_2O_2 ring (dihedral angle of 15.8(4)° between the O-Cu-O planes). The coordination of the copper(II) is a distorted tetragonal pyramid with the weakly coordinated water (Cu-O, 2.394(6)Å), in the apical position. The pyridine nitrogen (2.010(5)Å), amide nitrogen (1.919(5)Å), and alkoxide oxygen (1.951(4)Å) of one ligand and the alkoxide oxygen of the second ligand occupy the basal coordination positions. The magnetic susceptibility data that were previously reported[1] for this compound are discussed in terms of exchange coupling within the Cu_2O_2 ring of the dimer and through the hydrogen bonding network. The coupling is weak (μ_{eff} = 1.48 at room temperature) as expected from the non-planar nature of the ring[2] and the angle[3] at the bridging oxygen (98.3°).

Oxygen-Bridged Iron(III) Complexes

The preparations, structures, and magnetic properties of two five-coordinate iron(III) salicyaldimine complexes were reported.[4] The structure of the complex with N-(3-hydroxypropyl)salicylaldimine (SALPA), Fe(SALPA)Cl was refined to a conventional R value of 0.099, contains dimeric, five-coordinate

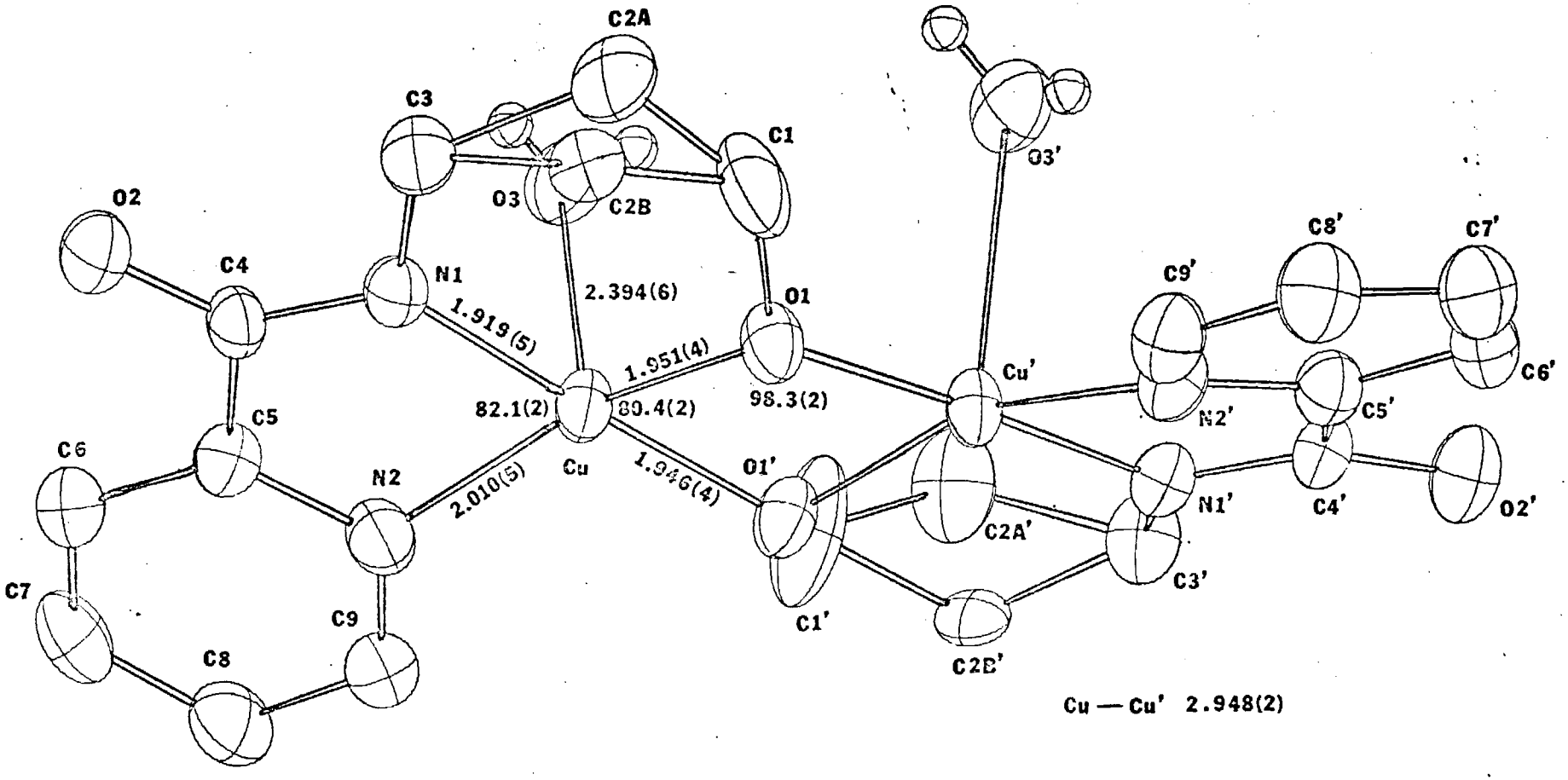

C2A
C3
C1
O3'
O2
O3
C2B
C8'
C7'
C4
N1
2.394(6)
O1
C9'
1.919(5)
1.951(4)
Cu'
C6'
82.1(2)
89.4(2)
98.3(2)
C5
N2'
C5'
C6
N2
2.010(5)
Cu
1.946(4)
O1'
N1'
C4'
O2'
C2A'
C7
C3'
C9
C1'
C8
C2B'
Cu — Cu' 2.948(2)

Figure 1

iron complexes in which the coordination is intermediate to the trigonal-bipyramidal and square-pyramidal arrangements. The room temperature magnetic moment is below the expected value for a high-spin d^5 complex and is indicative of antiferromagnetic coupling. The structure of the monomeric complex with N-(2-phenylethyl)salicylaldimine (SANE), $Fe(SANE)_2Cl$, was refined to a conventional R value of 0.074. It contains monomeric five-coordinate complexes in which the coordination is intermediate to the trigonal-bipyramidal and square-pyramidal arrangements. Above 196°K, the magnetic moment is typical for a high-spin d^5 complex. The magnetic moment at temperatures of 140°K and lower is greatly reduced and a phase transition is thought to occur between 140 and 196°K. The possibility of dimer formation at the temperature of the phase transition is suggested and would account for the change in magnetic moment.

The dimeric, five-coordinate complex, $[Fe(SALPA)Cl]_2$, reacts readily with sodium peroxide to give a red crystalline product, $[Fe_2(SALPA)_2(SALPAH)_2]$, which exhibits antiferromagnetic behavior (μ_{eff} per g. atom of iron = 4.45 B. M. and 2.34 B. M. at 298°K and 77°K, respectively). The three-dimensional x-ray crystal structure analysis of the toluene solvate of the complex revealed the presence of six-coordinate iron atoms, Figure 2, linked closely by bridging propoxide groups into dinuclear units having a planar, four-membered Fe-O-Fe-O ring (Fe-O = 1.93(2), 2.00(2)Å; O-Fe-O = 70.9(8), 70.2(8); Fe-O-Fe = 108.2(9), 110.6(9). Hydrogen bonding between the uncoordinated alcohol groups and the phenolic oxygens connects the dimeric units into infinite, doubly-linked chains. The iron atoms have virtually identical geometries (distorted octahedron with trans-nitrogens, two bridging cis μ-2 oxygens, two terminal oxygens); the iron atoms are nevertheless non-equivalent since the two bridging propoxide

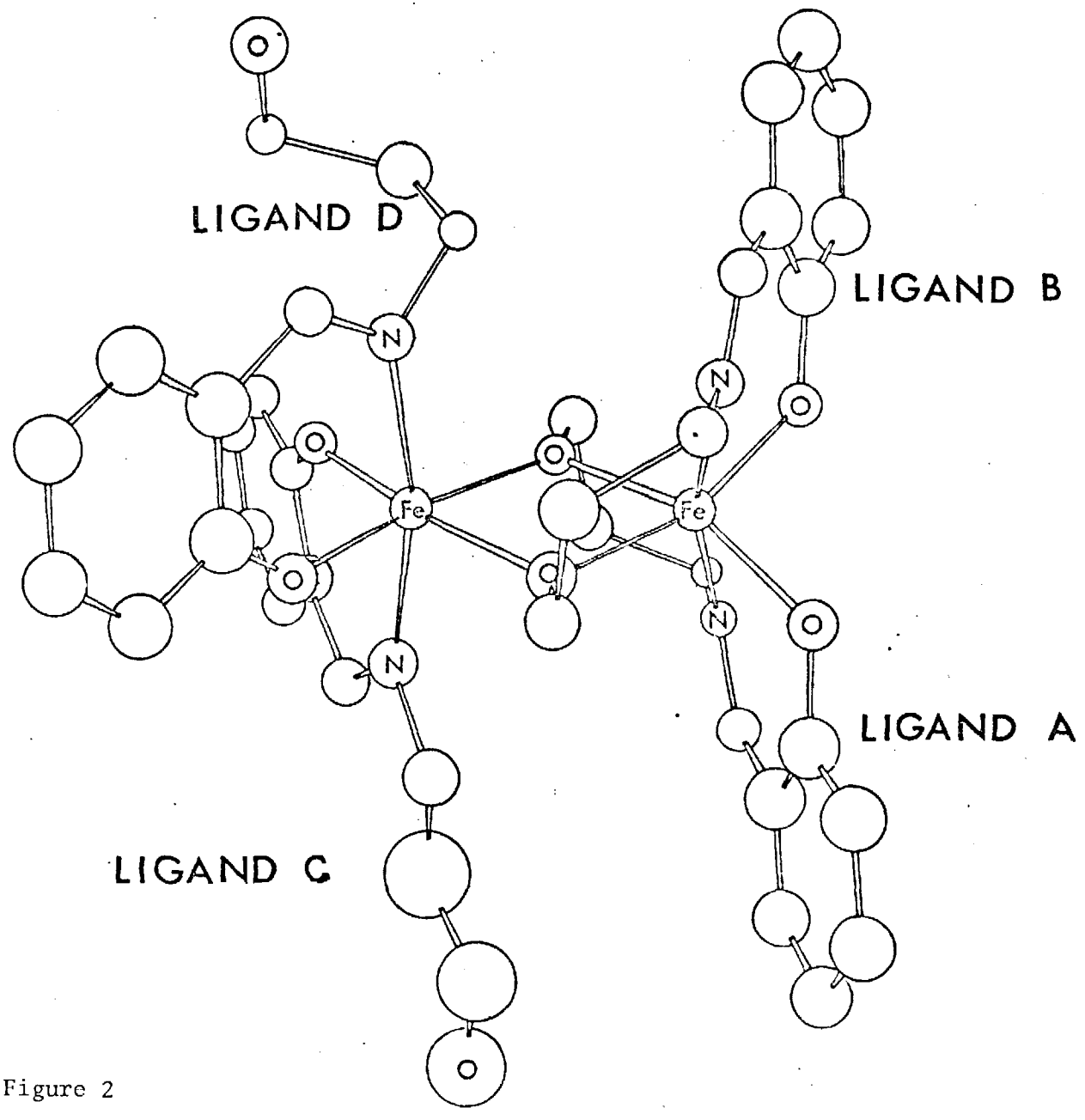


Figure 2

groups are chelated to the same iron atom.

Hydrogen-Bonded Complexes

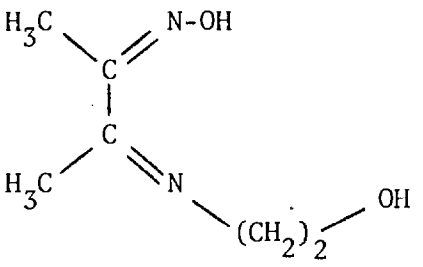
We have prepared and studied[5] a binuclear copper(II) complex in which the copper ions are bridged by hydrogen bonded O-H-O bridges with a copper-copper distance of 5.0 Å; although the copper-copper distance rules out direct exchange and the hydrogen bridged arrangement makes a π pathway unlikely, the magnetic properties of the compound indicate antiferromagnetic coupling. This example, thus, provides evidence for indirect exchange via a σ pathway. We have also prepared and studied the corresponding nickel(II) complex and found it to be isostructural with the copper(II) complex; in fact, the only significant differences in the two structures were the C-CH_3 distances (1.53 Å and 1.52 Å for the nickel compound).

The only previous example of cooperative hydrogen bonding in transition metal complexes was a cobalt(III)-nickel(II) complex[6] with 2-aminoethanol ligands which involved hydrogen bonding between octahedral faces of the two complexes. We have now determined the structure of the perchlorate salt of the corresponding nickel(II)-nickel(II) complex.[7] The structure is very similar to that of the cobalt(III)-nickel(II) compound; although an additional proton is necessary for charge balance, no effect of that proton on the structure has been detected. The compound shows a slight decrease in magnetic moment at lower temperatures but more complete magnetic studies will be necessary; similar compounds with a variety of metal ions have been prepared and all except the copper(II)-copper(II) compound are isostructural.

Oxime-Bridged Copper(II) Complexes

An unusual dimeric structure has been revealed by a single-crystal

x-ray diffraction study of $CuL(ClO_4)(H_2O)$[8] (where L represents the anion of 2-(2-hydroxyethyl)imine-3-oximebutane, II). The structure has been



II

refined by full-matrix least squares refinement to unweighted (R) and weighted (R_w) residuals of 0.057 and 0.056, respectively, for the 1579 reflections above background ($I \geq 3\sigma(I)$). The dimer, Figure 3, contains a centro-symmetric, nearly-planar six-membered ring formed by two copper atoms and two oxime (NO) groups. The Cu-N(oxime) and Cu-O(oxime) distances, 1.987(5) and 1.870(4)Å, respectively, indicate very strong coordination by both atoms of the oxime group, while the angles at N(oxime), Cu-N-O = 129.4(3)°, and at O(oxime), Cu-O-N = 121.9(3)°, are indicative of essentially sp^2 hybridization for the oxime atoms. The square-planar coordination of each copper atom is completed by a nitrogen atom (Cu-N = 1.928(5)Å) and an oxygen atom (Cu-O = 2.038(5)Å) of the tridentate ligand; there are also weak axial contacts to the water molecule (Cu-O = 2.492(6)Å) and the perchlorate group (Cu-O = 2.89(1)Å). The magnetic moment of zero (the compound shows only temperature independent paramagnetism) is ascribed to superexchange through the N-O bridges. Another compound that has an oxime bridge is dimeric bis(dimethylglyoximato)copper(II); in that compound, the six-membered ring is non-planar (chair conformation) and the magnetic moment is normal. A copper(II) complex now being studied has an intermediate moment and oxime bridges are probably present in that compound as well. This group of compounds and oxime-bridged complexes of other metal

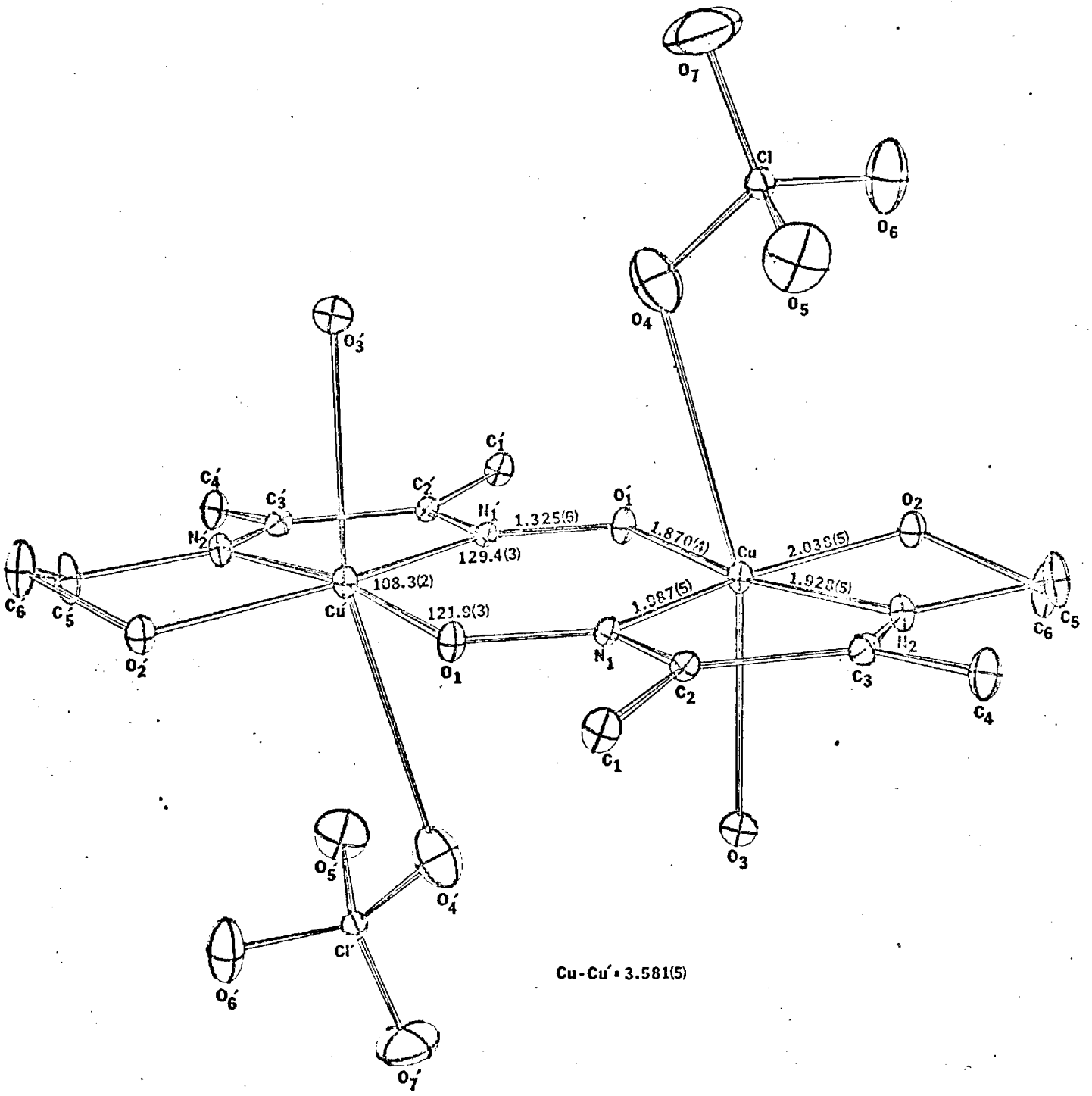
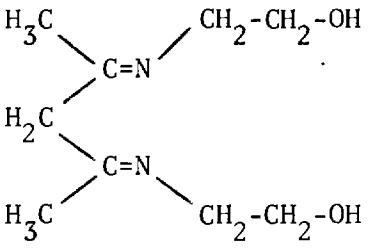

O7
Cl
O6
O5
O4
O3
C1
C4
C3
C2
N1
1.325(5)
O1
1.870(2)
Cu
2.038(5)
O2
129.4(3)
108.3(2)
1.987(5)
1.928(5)
C6
C5
C6
C5
O2
Cu
121.9(3)
O1
N1
N2
C3
C2
C1
O3
O5
O4
Cl
O6
O7
Cu-Cu = 3.581(5)

Figure 3

ions should provide new insights into the mechanism of spin exchange.

Mononuclear Complexes

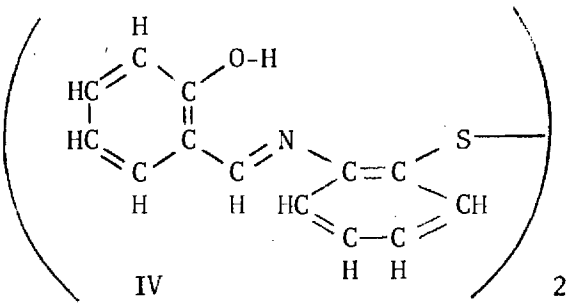
A cobalt(III) complex of N,N'-di(2-hydroxyethyl)-2,4-pentanediimine, III,



III

has been prepared from bis(2,4-pentanedionato)cobalt(II) and 2-aminoethanol and the structure of the complex has been determined by an x-ray diffraction study. The structure, Figure 4, was refined to a conventional R value of 0.060 and consists of a cobalt(III) ion coordinated to the planar, tetradentate diimine ligand and to two monodentate 2-aminoethanol groups. The coordination geometry shows only small deviations from ideal octahedral geometry with the cobalt-donor atom distances ranging from 1.897(4) to 1.989(3)Å and the angles at cobalt for cis-donor atoms ranging from 85.5° to 94.6°.

Chloro(bis{o-salicylideniminephenyl}disulfido)iron(III), $Fe(C_{26}H_{18}N_2S_2O_2)Cl$, has been prepared and its crystal structure determined from precession camera data. The structure, Figure 5, was refined to a conventional R value of 0.096 by full-matrix least-squares refinement and consists of monomeric iron(III) complexes with octahedral coordination. The disulfide, IV, functions as a



IV 2

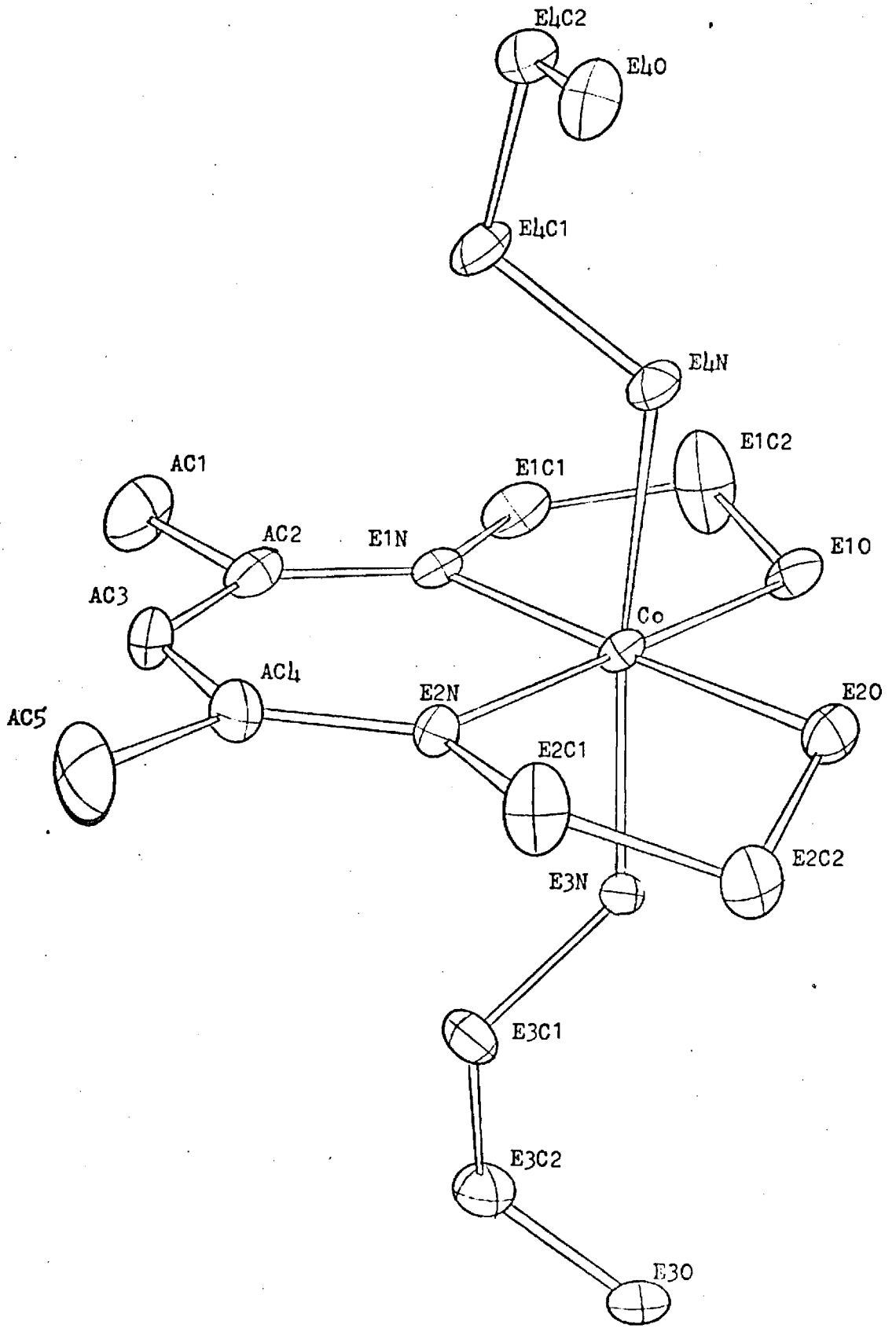

E4C2
E4O
E4C1
E4N
E1C2
AC1
E1C1
AC2
E1N
E1O
AC3
Co
AC4
E2N
E2O
AC5
E2C1
E2C2
E3N
E3C1
E3C2
E3O

Figure 4

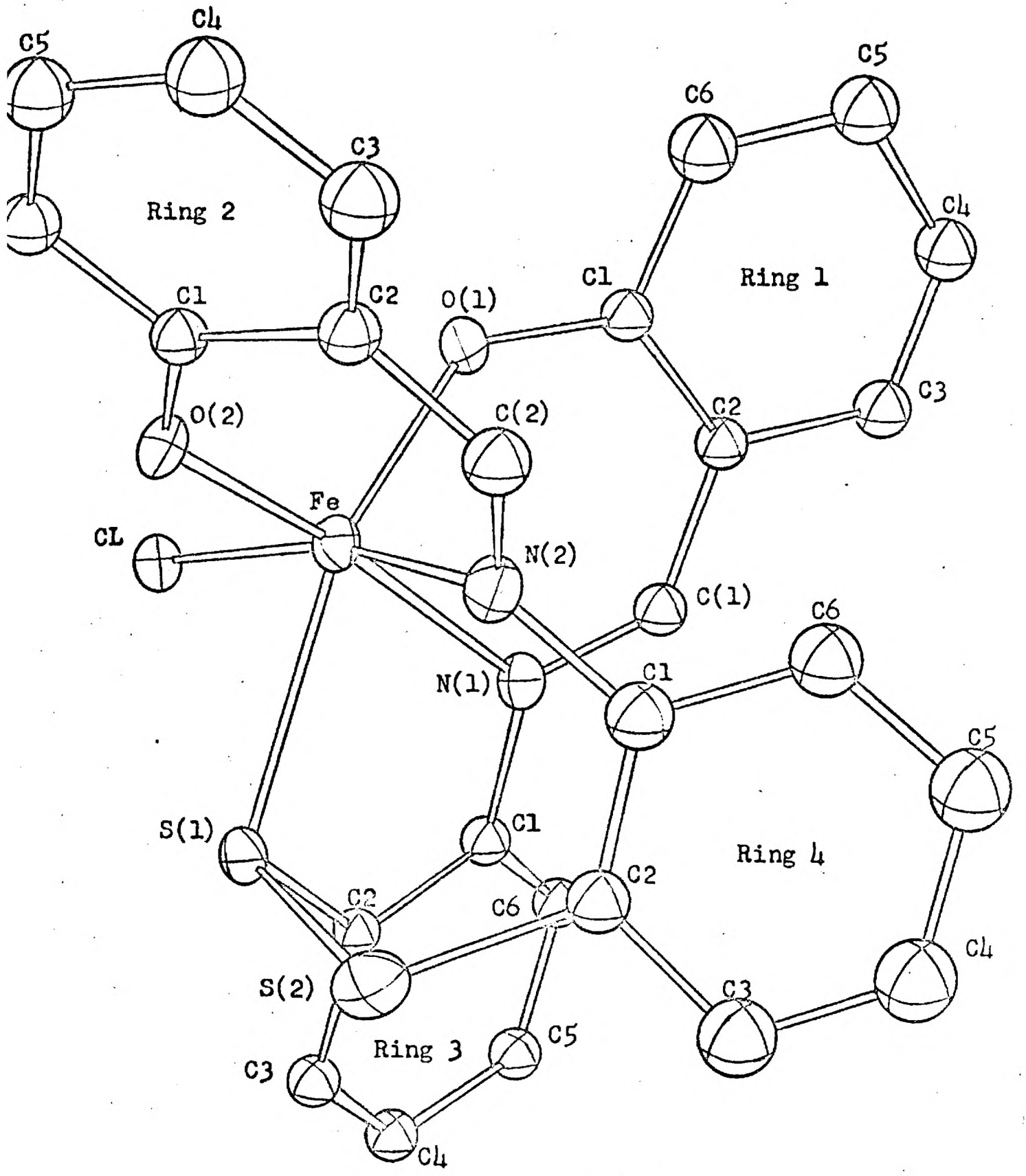

C4
C5
C3
Ring 2
C1
C2
O(1)
O(2)
C(2)
Fe
CL
N(2)
C(1)
N(1)
S(1)
C1
C2
C6
S(2)
C5
C3
C4
C5
C6
C4
Ring 1
C1
C3
C2
C6
C1
C5
Ring 4
C2
C4
C3
Ring 3
C5
C3
C4

Figure 5

pentadentate ligand and is coordinated through two nitrogens, two oxygens, and one sulfur atom; the chloride ion occupies the sixth coordination position. The magnetic moment, 5.90 B.M., is normal for a high-spin octahedral iron(III) complex.

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Final Technical Report

NSF GP-20885

Polynuclear Complexes of First-Row Transition Metal Ions

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Introduction

Although a number of polynuclear complexes have been studied in the last few years, there is little understanding of the factors favoring the formation of polynuclear (rather than mononuclear) complexes, the factors determining the structures of the polynuclear complexes, or the relationship between structures and properties of such complexes. In order to reach a better understanding of these complexes, we have synthesized and studied a variety of complexes and these studies are summarized in a recent review[1].

Table I

Abbreviations Used for Ligands

acac	the anion of 2,4-pentanedione
Deta	the anion of diethanolamine
DiimH	the dianion of the diimine of 2,4-pentanedione and 2-aminoethanol
EIA	the dianion of the imine of 2,4-pentanedione and 2-aminoethanol
Eta	the anion of 2-aminoethanol
Salpa	the dianion of the imine of salicylaldehyde and 3-amino-1-propanol.

Oxygen-Bridged Complexes with Aminoalcohols as Ligands

Cobalt complexes with aminoalcohols as ligands have been known[2,3] for many years and are of interest because most of the compounds contain both divalent and trivalent cobalt. Generally, several different compounds can be prepared from the same aminoalcohol and the nature of the product depends on the ligand-to-metal ratio, the anion(s) present, and the pH of the solution.

With 2-aminoethanol, both dinuclear, $[Co_2(Eta)_3(H_2O)_3]^{2+}$, and trinuclear, $[Co_3(Eta)_6]^{2+}$, species have been reported[2-5]. Three different isomers of the trinuclear species are possible because of the optically active $Co(Eta)_3$ units which serve as ligands for the central cobalt(II) ion. The structure of one crystal, Figure 1, has been determined

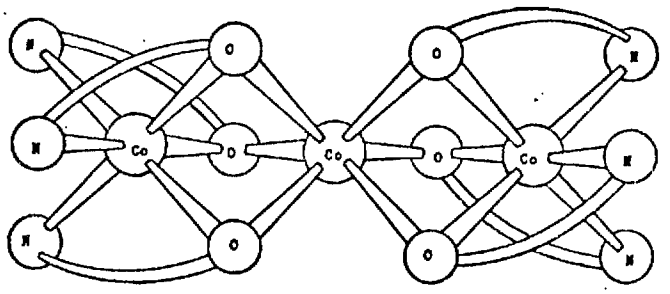


Figure 1

and that structure revealed trigonal-prismatic coordination of the central cobalt(II) for one of the optically active isomers. Similar trinuclear complexes of the type $[MCo_2(Eta)_6]^{2+}$ (where M represents zinc(II), nickel(II), copper(II), or magnesium(II)) and $[Co_3(Eta)_6]^{3+}$ have been prepared and are being studied.

A number of cobalt complexes of diethanolamine (2,2'-iminodiethanol)

have been prepared[2,7,8] and a number of these contain both divalent and trivalent cobalt. The structure of a tetranuclear complex, $Co_4(Deta)_2$-$(Deta\ H)_4(ClO_4)_2$ has been determined and is illustrated in Figure 2a. The bridging arrangement is similar to that found[9] for a mixed-valence cobalt complex of a binucleating ligand, Figure 2b, and that found for several titanium alkoxides[10-12]. The cobalt(II) ions of the complex with

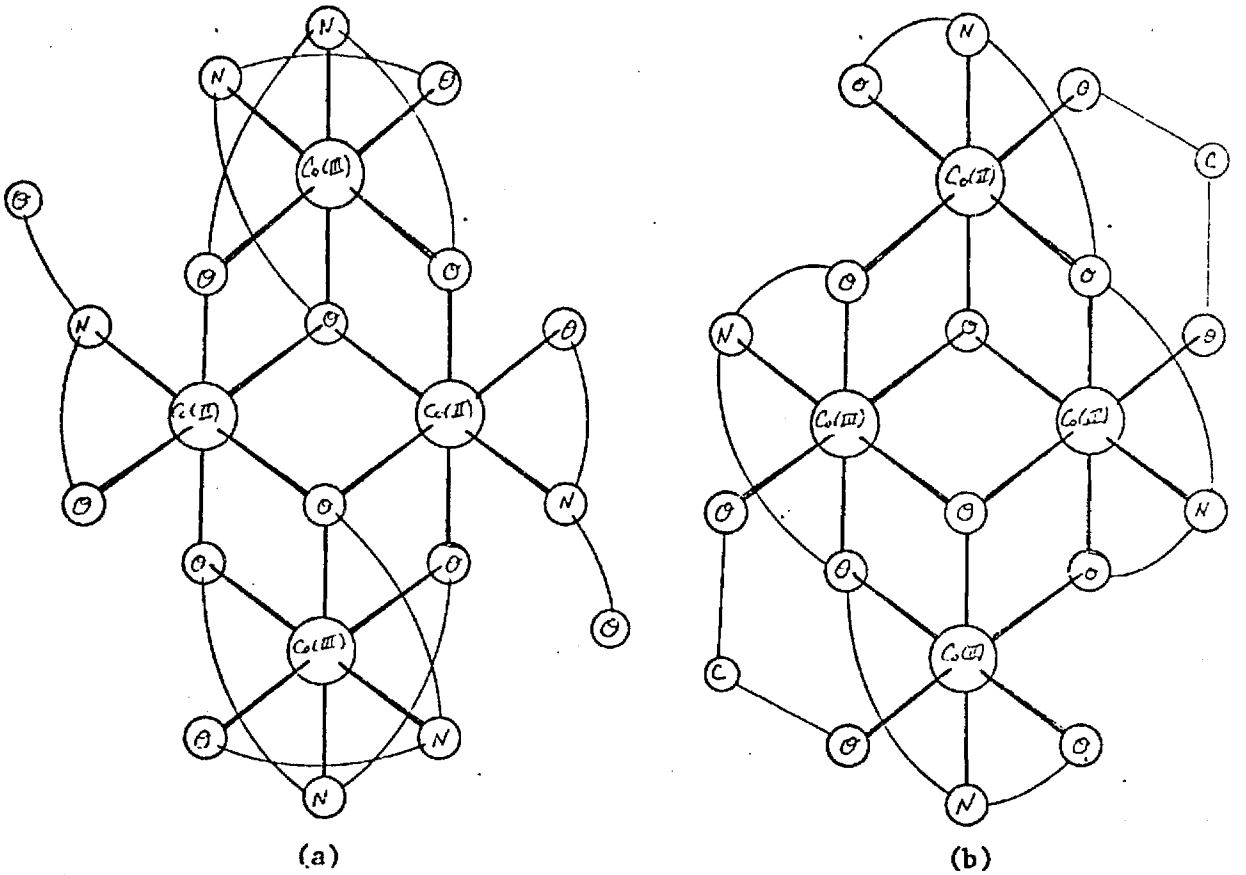


Figure 2

the binucleating ligand are at opposite ends of the structure and the compound exhibits simple paramagnetic behaviour. The cobalt(II) ions of the diethanolamine complex form the central four-membered ring and slight antiferromagnetic behaviour is observed; this arrangement of cobalt(II) ions is similar to that found for the mixed-valence cobalt compound,[13]

$[Co_4(Acac)_4(CH_3O)_4(C_2H_3O_2)_2]$, in which the cobalt(II) ions of the cubane-type structure are in a four-membered ring and show antiferromagnetic coupling.

There have also been reports of polynuclear complexes of copper(II) with a number of substituted 2-aminoethanols. These compounds, which have the empirical formula $Cu(OCH_2CH_2NR_2)X$, have been investigated by several groups.[14-18] Uhlig and coworkers[16] divided the compounds into three categories on the basis of magnetic properties and the extent of molecular association. Compounds in the first group were described as dimeric species with four-coordinate copper(II) ions and they exhibited magnetic moments, 0.60 to 1.23 B. M. at room temperature, that were greatly reduced from the spin-only value, 1.73 B. M., for one unpaired electron. The second group of compounds showed higher degrees of association, approaching tetrameric values in concentrated solution, and exhibited normal magnetic moments around 1.9 B. M. at room temperature. Compounds in the third group exhibited intermediate moments and also appeared to be tetrameric.

The structure of a compound with properties similar to those of compounds of the first type has been reported. The structure of $Cu(OCH_2CH_2NH_2)Br$, revealed planar four-coordinate copper(II) ions bridged by alkoxide groups into dimeric units with a planar four-membered copper-oxygen ring. The copper-copper distance was 3.03Å. A complex of 3-amino-1-propanol. $Cu(OCH_2CH_2CH_2NH_2)(H_3CCO_2)$, has recently been prepared[19] and was found to have an extremely low room temperature magnetic moment, 0.41 B. M. per g. at. of copper. The structure, Figure 3, contains square-planar copper(II) ions, monodentate acetate groups, and alkoxide groups bridging the metal ions to form a dimer with a planar four-membered ring; the copper-copper distance is 3.012Å.

Copper(II) complexes with anions of aliphatic diaminealcohols,

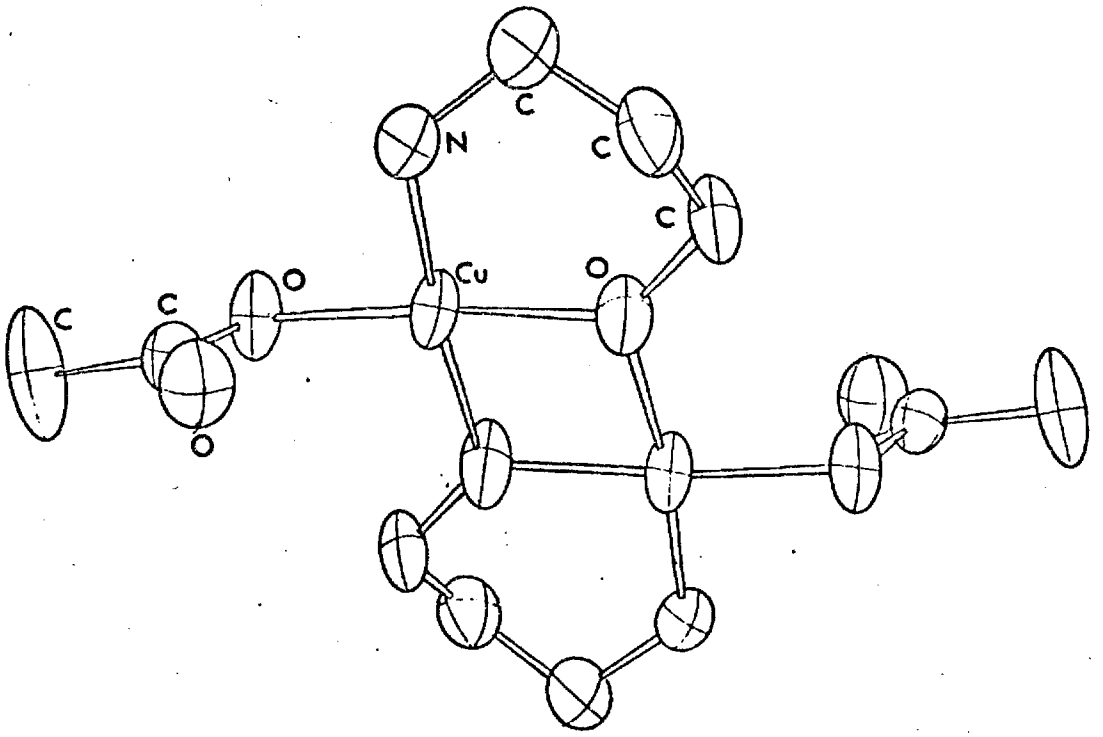


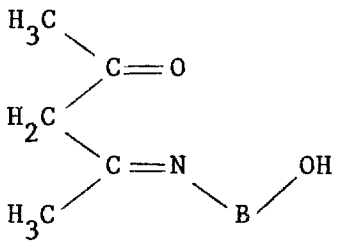
Figure 3

NH_2-$(CH_2)_m$-NH-$(CH_2)_n$-OH, have been reported.[20-22] The 1:1 complex of N-(α-hydroxypropyl)trimethylenediamine (m=3, n=3) was found to have a normal moment (1.79 B. M.), the 1:1 complex of N-(α-hydroxypropyl)ethylenediamine (m=3, n=2) was found to have a low moment (0.90 B. M.), and no complex was isolated for N-(β-hydroxyethyl)ethylenediamine (m=2, n=2). A tetrameric cubane-type structure was assigned to the normal-moment compound and a dimeric structure was assigned to the low-moment compound. Trinuclear complexes with the formula $[Cu_3\{R_2N(CH_2)_2NH(CH_2)_3O\}_2(OH)_2](ClO_4)_2$ (R = CH_3, C_2H_5) have also been reported. These compounds have magnetic moments that are temperature dependent but at low temperatures the values correspond to one unpaired electron per trimer; a linear arrangement of edge-sharing copper(II) units is

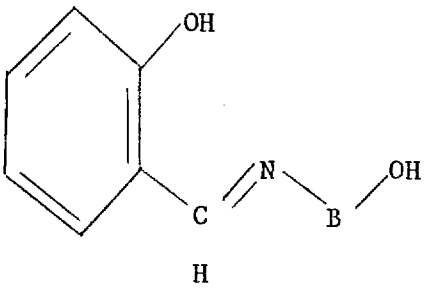
postulated.

Oxygen-Bridged Complexes with Iminoalcohols as Ligands

Most Schiff base ligands formed from aminoalcohols have been prepared from 2,4-pentanedione or from salicylaldehyde and the resulting ligands are represented by I and II, respectively. Magnetic properties have been reported for a number of these complexes and several structure determinations have been carried out.



I



II

One of the earliest copper(II) complexes of this type to be characterized by a complete structure determination[23] was the 1:1 complex with acetylacetone-o-hydroxyanil, I (B = C_6H_4). The tetrameric complex has a step-like structure, Figure 4, (only metal ions and coordinated atoms

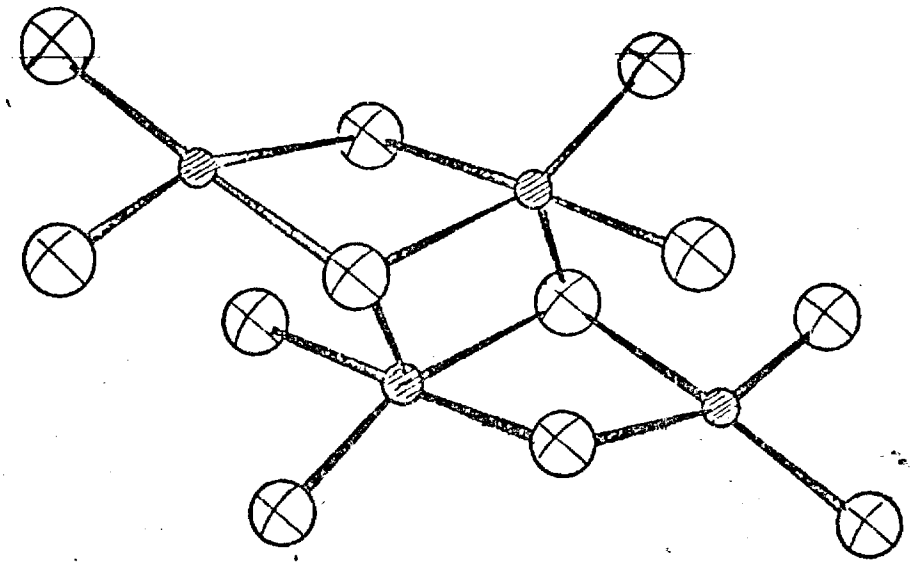
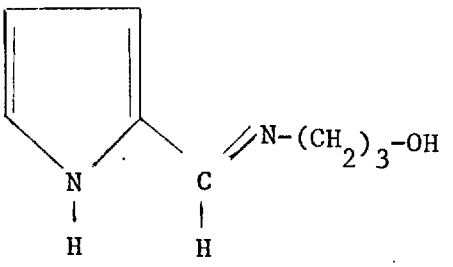


Figure 4

are indicated) and contains copper(II) ions with square-planar and square-pyramidal coordination. The structure can be thought of as two dimers connected by additional copper-oxygen interactions and early discussions of the magnetic properties of this compound and compounds with related ligands, II, (B = C_6H_3R) employed the formula derived for dimeric units.[24] However, more recent reports[25] have shown that the experimental magnetic data cannot be fit by the dimer formulation but a good fit can be obtained for the tetrameric structure. Due to the interaction that forms the tetramer, there are two types of bridging oxygens (three-coordinate planar and four-coordinate tetrahedral) and there are two types of four-membered copper-oxygen rings. There are also two copper-copper distances, 2.99Å within the dimeric unit and 3.27Å between the five-coordinate copper(II) ions.

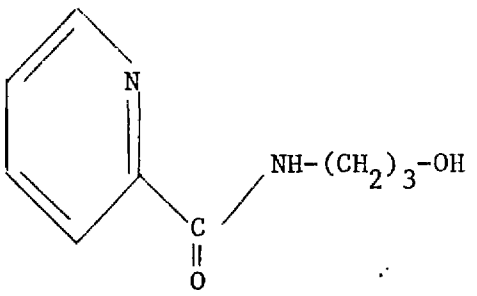
Several examples of dimeric copper(II) complexes with imine ligands of types I and II have been reported[26-31] and a complex of the Schiff base, III, of pyrrole-2-carboxaldehyde has also been described.[32] The structure studies that have been reported[26,27,32] have revealed planar, four-membered rings similar to those observed for the aminoalkoxide dimers discussed earlier. Complexes represented by the formula CuL, where L represents the dianion formed by removing two protons from I (B = $-CH_2CH_2CH_2-$) or III, contain four-coordinate copper(II) and exhibit extremely low magnetic



III

moments (ca. 0.5 B. M. per g. at. of copper) at room temperature. A complex represented by the formula Cu(Salpa H)Cl contains five-coordinate copper(II) and has a somewhat higher magnetic moment at room temperature (1.1 B. M. per g. at. of copper). Since only one proton has been removed from the ligand and the phenolic oxygen is the bridging group, the remaining proton is assumed to be on the alcohol oxygen. The copper-copper distance in that compound is 3.29Å and the ring is unsymmetrical with Cu-O distances of 1.78Å and 2.22Å.

Two copper(II) compounds that were reported[33] recently contain a somewhat different ligand, IV; the anhydrous compound has a low room temperature



IV

magnetic moment and the temperature susceptibility could be described by the equation for dimeric units with $2J = -550$ cm^{-1} and g - 2.14.[34] However, the room temperature moment of the dihydrate is considerably higher, 1.51 B. M., and it was reported that the temperature dependence of the susceptibility could not be fit by the dimer equation. A structure determination[35] for the dihydrate (R = 0.043) has revealed a dimeric unit, Figure 5, with a bent four-membered copper-oxygen ring (the dihedral angle between the two O-Cu-O planes is 15.8°). The copper-copper distance is 2.942Å. The copper was found to be five-coordinate with a water molecule occupying the axial position of a distorted tetragonal

pyramid. The dimeric units are connected by weak hydrogen bonding (O-O distance of 2.84Å) and exchange interactions through the hydrogen-bonded network may be responsible for the deviation of the susceptibilities measured

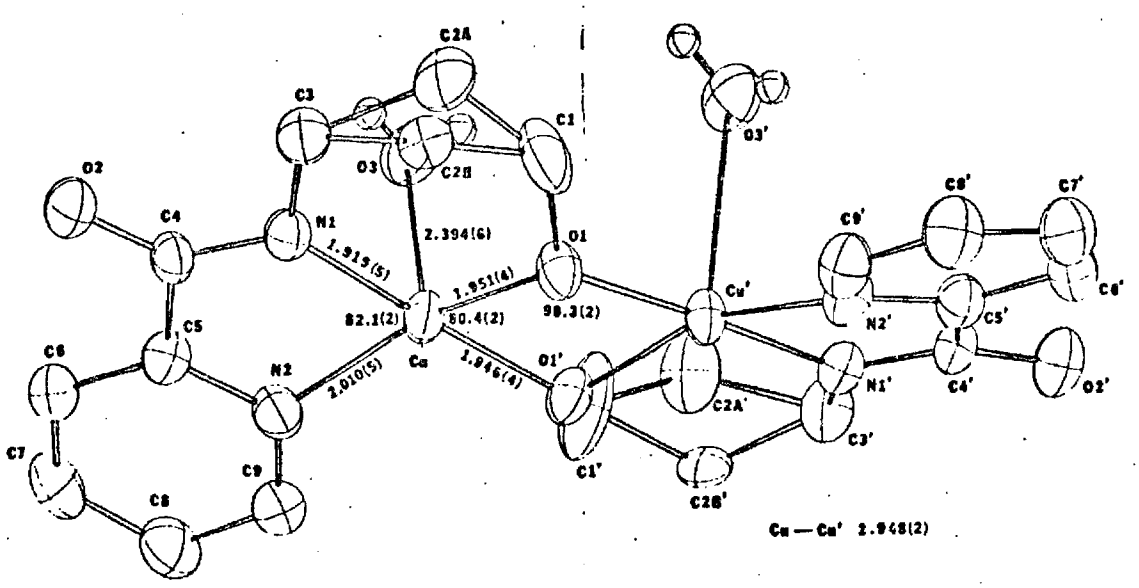


Figure 5

at different temperatures from the values calculated for a dimer.

A tetrameric structure has been reported[26] for the copper(II) complex of the ligand, I (B = C_2H_4), prepared from 2,4-pentanedione and 2-aminoethanol. The structure is of the cubane type, Figure 6, and contains five-coordinate copper(II) and four-coordinate oxygens. The structure contains two types of four-membered copper-oxygen rings with copper-copper distances of 3.006Å and 3.259Å. The room temperature magnetic moment is normal, 1.87 B. M., and very low temperatures (below 50°K) are necessary to observe the effect of coupling in this compound.[36]

A nickel complex of this same ligand (I, B = C_2H_4) is dimeric[37] with a bent four-membered nickel-oxygen ring (the dihedral angle between O-Ni-O planes is 38.8°); the nickel-nickel distance is 2.690Å and the internal angles are

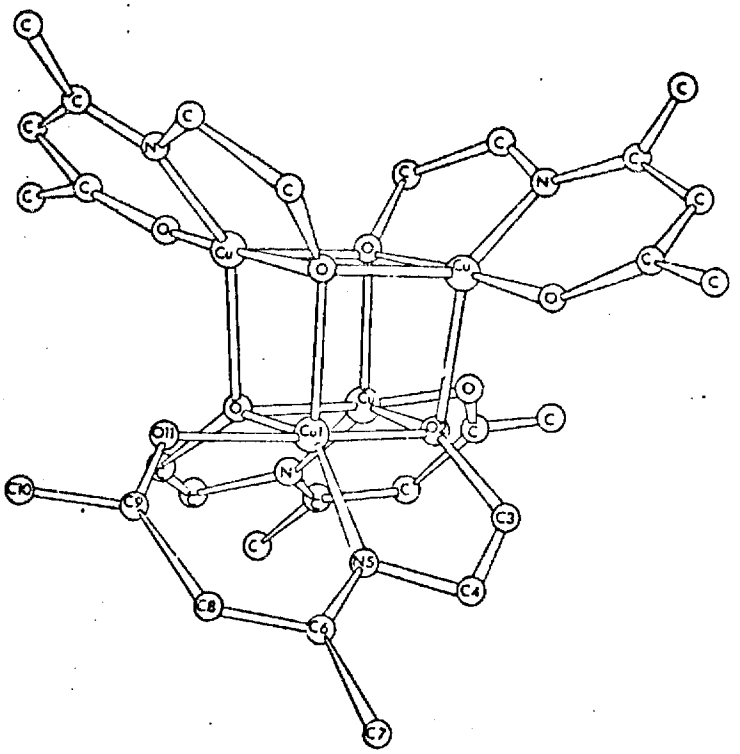


Figure 6

80.4° at nickel and 92.2° at oxygen. The nickel is planar and four-coordinate and the compound shows only temperature independent paramagnetism.

Iron(III) complexes with iminoalcohol ligands of types I and II have been prepared and studied;[38-40] all of these complexes show antiferromagnetic coupling with -J values in the range 10-20 cm^{-1}. A structure determination[38,39] for the complex of II (B = $-(CH_2)_3-$) revealed dimeric units of $[Fe(Salpa)Cl]_2$, Figure 7, containing five-coordinate iron(III) and a planar four-membered ring. The iron-iron distance is 3.09Å and the internal angles are 75.9° at iron and 104.1° at oxygen. The coordination of the metal ion in this compound is best described as square pyramidal in contrast to the trigonal bipyramidal coordination found for the copper complex of the same ligand. The ligand is present in the iron complex as the dianion but in the copper complex

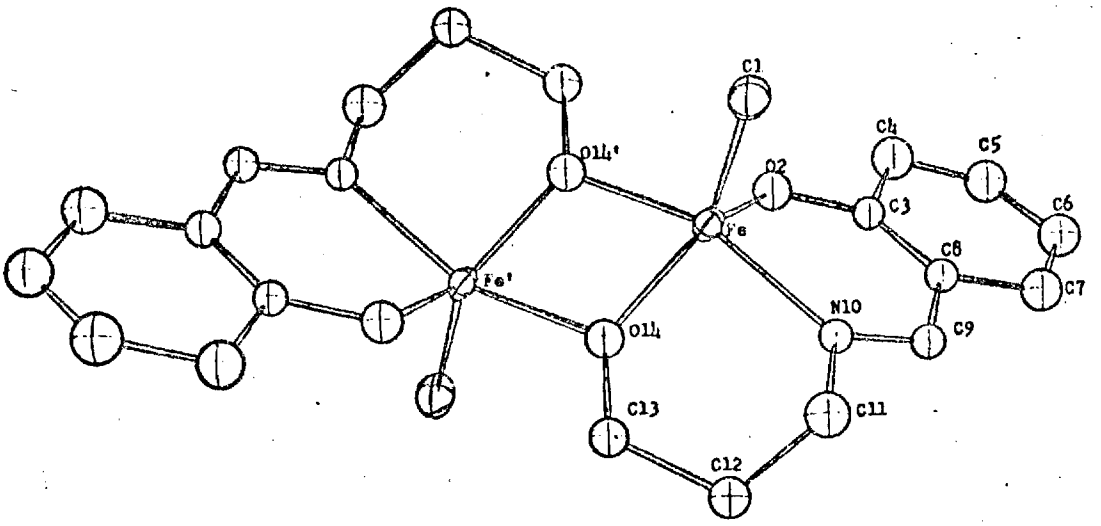


Figure 7

only one proton has been removed. The two structures also differ in the bridging group since in the iron compound the alkoxide oxygen serves as the bridge but in the copper compound the bridging group is phenoxide oxygen.

By reacting $[Fe(Salpa)Cl]_2$ with base, a compound which was formulated as Fe(Salpa)(Salpa H) was obtained.[40] Although initially expected to be monomeric, the compound exhibited antiferromagnetic behaviour and a structure study revealed dimeric units with six-coordinate iron(III), Figure 8. One iron ion is chelated by two tridentate dianion ligands (A & B in Figure 8) and the alkoxide groups of these two ligands serve as bridging groups to the second iron. The octahedral coordination of the second iron is completed by the two remaining ligands (C and D in Figure 8), each singly charged, coordinating through the imine nitrogen and the phenoxide oxygen. The alcohol groups of these two bidentate ligands are not coordinated but are involved in weak hydrogen bonding. Although there is no symmetry to require planarity, the four-membered iron-oxygen ring is essentially planar. The iron-iron distance, 3.22Å, is slightly longer than that of the five-

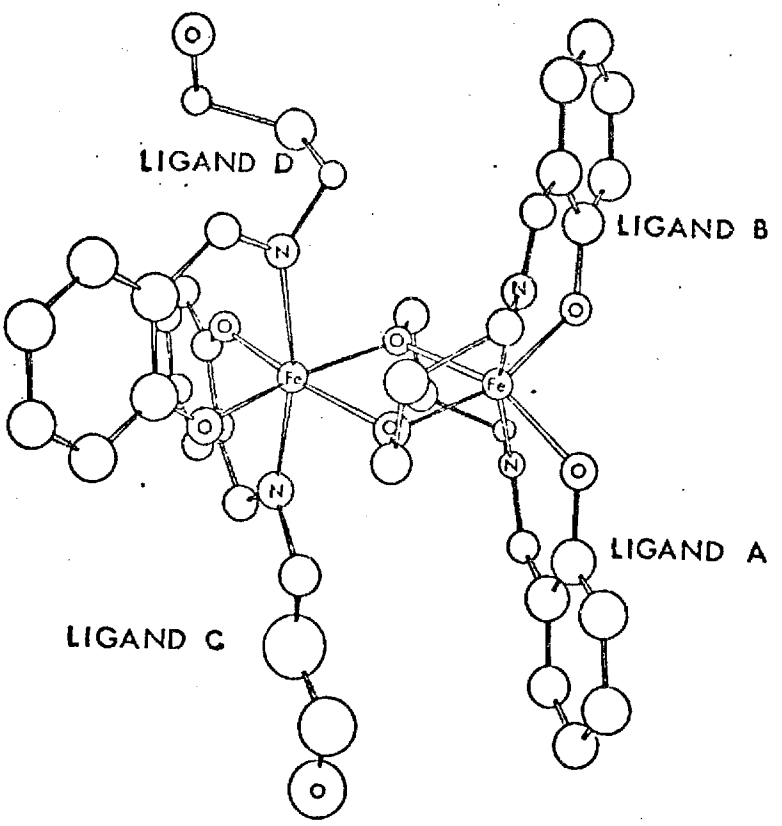


Figure 8

coordinate dimer. The internal angles of the ring are 70.2° and 70.9° at the iron atoms and 108.2 and 110.6 at the oxygen atoms.

Unusual magnetic properties indicative of antiferromagnetic behaviour have been noted for a number of the compounds discussed in this section and in the preceding section. In all of the compounds for which structural information is available, the metal-metal distance is sufficiently large to make direct coupling unlikely. Furthermore, for the copper(II) compounds (for which structural data are most abundant) there is no correlation between the copper-copper distance and the magnitude of the coupling constant; in

fact, the compound which shows the weakest coupling has one of the shortest copper-copper distances and the compound which shows the strongest coupling has one of the longest copper-copper distances. It is now generally accepted that the coupling in these compounds occurs by superexchange through the bridging groups but the mechanism or pathway of the exchange is still a matter of considerable discussion.

It is interesting that in both the four- and six-membered ring dinuclear compounds, stronger couplings are observed for the planar ring systems. On the basis of this observation for the four-membered ring compounds, the suggestion was made[26] that a π-pathway was responsible for coupling in these systems; the recent observation[35] of much weaker coupling in a bent four-membered ring compound is also consistent with this suggestion.

For a planar, four-membered ring, a π-system involving copper d_{xz},d_{yz} orbitals and oxygen p_z orbitals is possible. The projection of these orbitals onto the x-y plane is shown in Figure 9. When the O-Cu-O angle is 90°, the

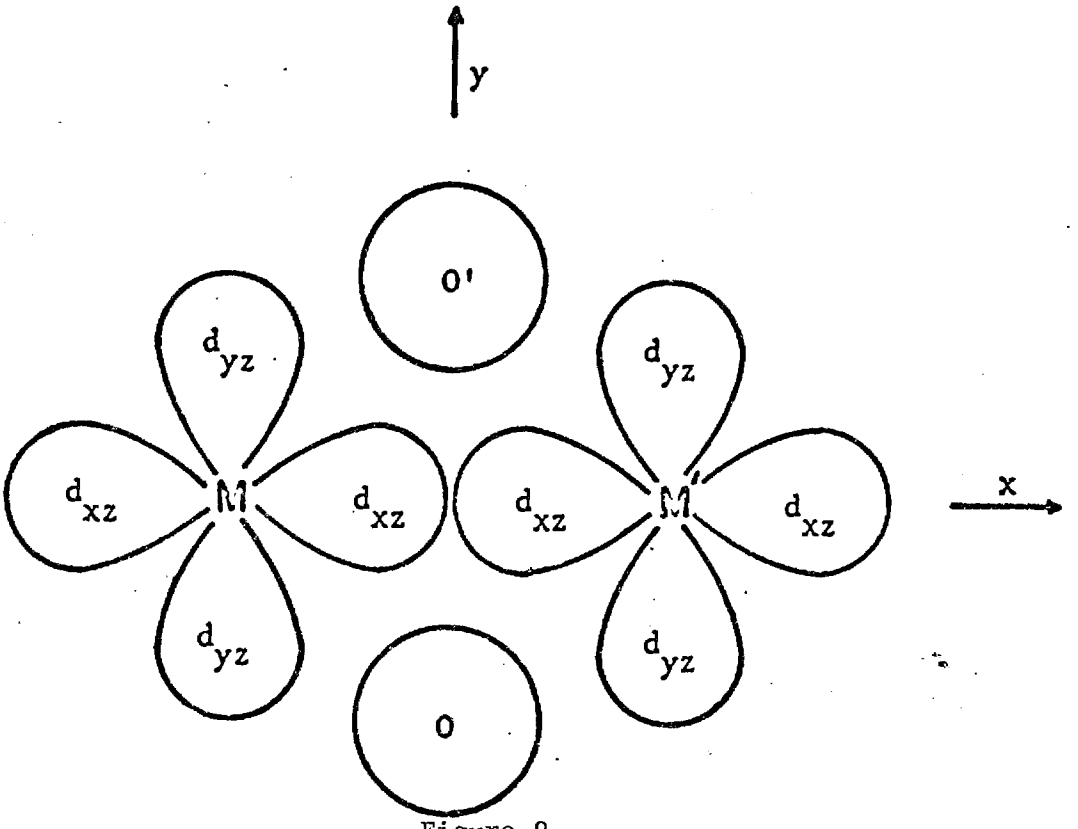


Figure 9

linear combination of k_{xz} orbitals and the linear combination of d_{yz} orbitals, although of different symmetries, have identical overlaps with the oxygen p_z orbitals. The resulting molecular orbitals, Figure 10, would then occur as pairs of equal energies. At O-Cu-O angles other than 90°, the d_{xz} and k_{yz} linear combinations would have different overlaps, the accidental degeneracy would be removed, and the energy difference would be a function of the angle at copper.

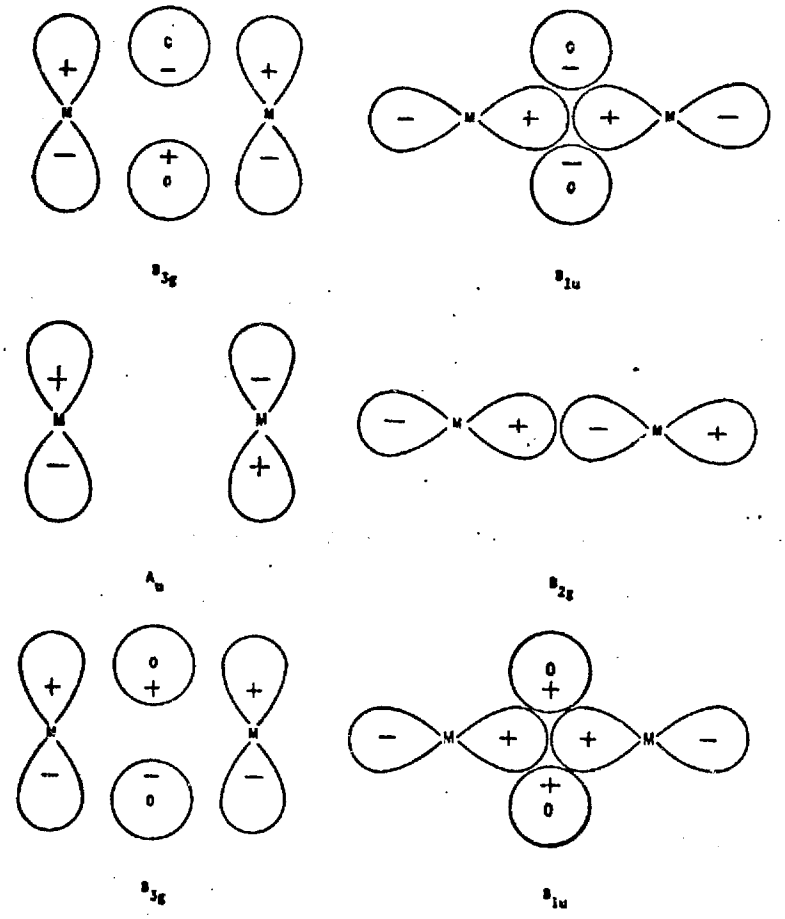


Figure 10

For a system which contains unpaired electrons only in the d_{xz} or the d_{yz} orbitals, a triplet ground state would be expected for an O-Cu-O angle

of 90° but a singlet ground state would be expected for angles other than 90°. However, for square-planar copper(II), the one unpaired electron on each copper would be in the d_{xy} orbital (or $d_{x^2-y^2}$ orbital, depending on the orientation of axes) and electron pairing through the π-system would occur only through mixing of states. As has been pointed out,[41] it is unlikely that such mixing would be sufficient to cause the coupling observed in the systems.

For hydroxy-bridged[42] and chloro-bridged[43] copper(II) compounds, an interesting linear relationship between the bond angle at the bridging group and the coupling constant has been observed and has been taken as evidence for a σ-pathway for the spin coupling. A molecular orbital treatment, similar to that used for the π-system, can be used to explain these observations. In a planar dimer with square-planar coordination of copper, the two half-filled d_{xy} orbitals would transform as linear combinations with g and u symmetries and these would interact with filled orbitals on the bridging groups. Considering only the p_x and p_y orbitals on the bridging groups, the pair of p_x orbitals and the pair of p_y orbitals, although of different symmetries, would have identical overlaps with the pair of d_{xy} orbitals, Figure 11, for a bridge angle of 90°. The two different symmetry combinations would, thus, give molecular orbitals of equal energies but distortion of the bridge angle away from 90° would destroy the acciental degeneracy. If the s-orbitals of the bridging group are considered, the picture is modified since these orbitals would mix into the molecular orbitals of u symmetry and make the two energies different for an angle of 90°. The accidental degeneracy would be expected to occur at some angle other than 90°. The plot of observed

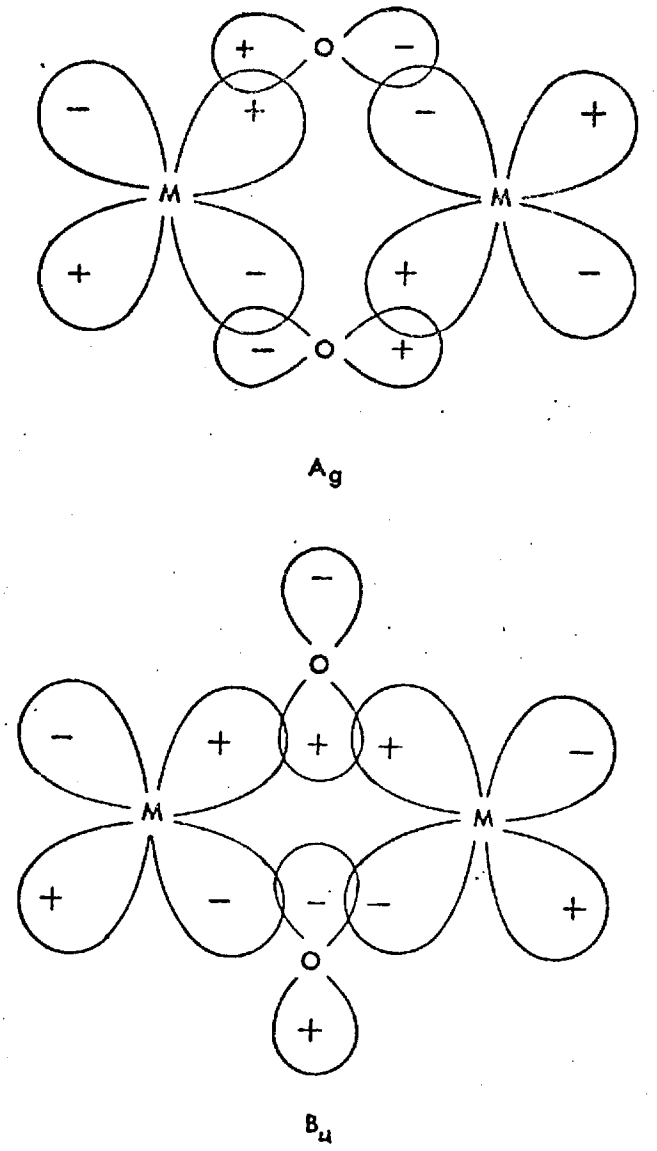


Figure 11

constants versus bridging angles for the hydroxy bridged complexes shows a 2J value of zero at about 97°.

Although couplings by the σ-mechanism and π-mechanism depend on different angles (O-Cu-O vs Cu-O-Cu), these angles are related in the four-membered ring

compounds and it is difficult to find conclusive evidence for either mechanism. However, the fact that the unpaired electrons should be in the d_{xy} orbital makes the σ-mechanism appear more important.

In reviewing the structures and magnetic properties of the oxygen-bridged copper(II) complexes, five types of structures can be identified:

1) Dimers with planar rings and four-coordinate copper. In all of these[15,19,26,32] the ring angle at copper is about 75° and the ring angle at oxygen is about 105°. The room temperature magnetic moments are around 0.5 B. M. and indicate large, negative coupling constants.

2) Dimers with planar rings and five-coordinate copper. Only one example of this type has been studied[27] and the angles of the ring are 69.7° and 110.3° at copper and oxygen, respectively. The room temperature magnetic moment of 1.1 B. M. is indicative of considerably weaker coupling.

3) Dimers with bent ring and five-coordinate copper. Only one example of this type has been studied.[35] The bent ring leads to a smaller ring angle at oxygen, 98.3°, and a larger angle at copper, 80.4°. The room temperature moment is 1.50 B. M.

4) Tetramers with a stepped structure and both four- and five-coordinate copper. Only one example of this type has been studied[23] by x-ray diffraction. Two of the bridging oxygens are three coordinate and their Cu-O-Cu angle is 100.7°; the remaining two bridging oxygens are four-coordinate with Cu-O-Cu angles of 97.1°, 89.5°, and 106.7°. The room temperature magnetic moment is 1.37 B. M. and the temperature dependent behaviour indicates[25] four coupling constants of -140, -48, 0, and 134 cm^{-1}. It is probable that the tetramers, $[Cu(OCH_2CH_2NR_2)X]_4$, reported by Uhlig to show intermediate moments,

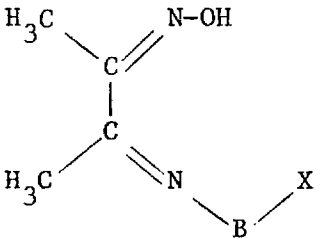
are also of this type.

5) Tetramers with a cubane-type structure and five-coordinate copper. Again, only one example has been completely characterized.[26] All bridging oxygens are four-coordinate and the Cu-O-Cu angles are 97.8°, 98.3°, and 97.6°. The room temperature magnetic moment, 1.84 B. M., is a normal paramagnetic value but at very low temperatures, coupling is observed. It is probable that the tetramer with normal moments reported by Uhlig are of this type.

In the case of the iron(III) complexes, with an unpaired electron in each of the five 3d-orbitals, both the σ-mechanism and the π-mechanism may be involved in the coupling. The only compounds discussed above[38-40] were planar-ring dimers with five- or six-coordinate iron and a coupling constant of about -17 cm^{-1}. In contrast to these compounds, with ring angles at oxygen of about 108°, the iron(III) dimer of N,N'-ethylene bis(salicylideneiminate) was reported to have a coupling constant of -7 cm^{-1} and a ring angle at oxygen of 104.5°. The lower coupling constant for a smaller angle at oxygen is consistent with the discussion of the coupling mechanisms.

Oxime-Bridged Complexes

An interesting series of ligands, V, can be prepared from



V

condensation reactions of 2,3-butanedione monoxime and the copper(II)

complexes of these ligands are presently being investigated. The ligands prepared from aminoalcohols (X = OH, B = C_2H_4 or $(CH_2)_3$) yield dimeric complexes[44,45], Figure 12, that are essentially diamagnetic because of strong

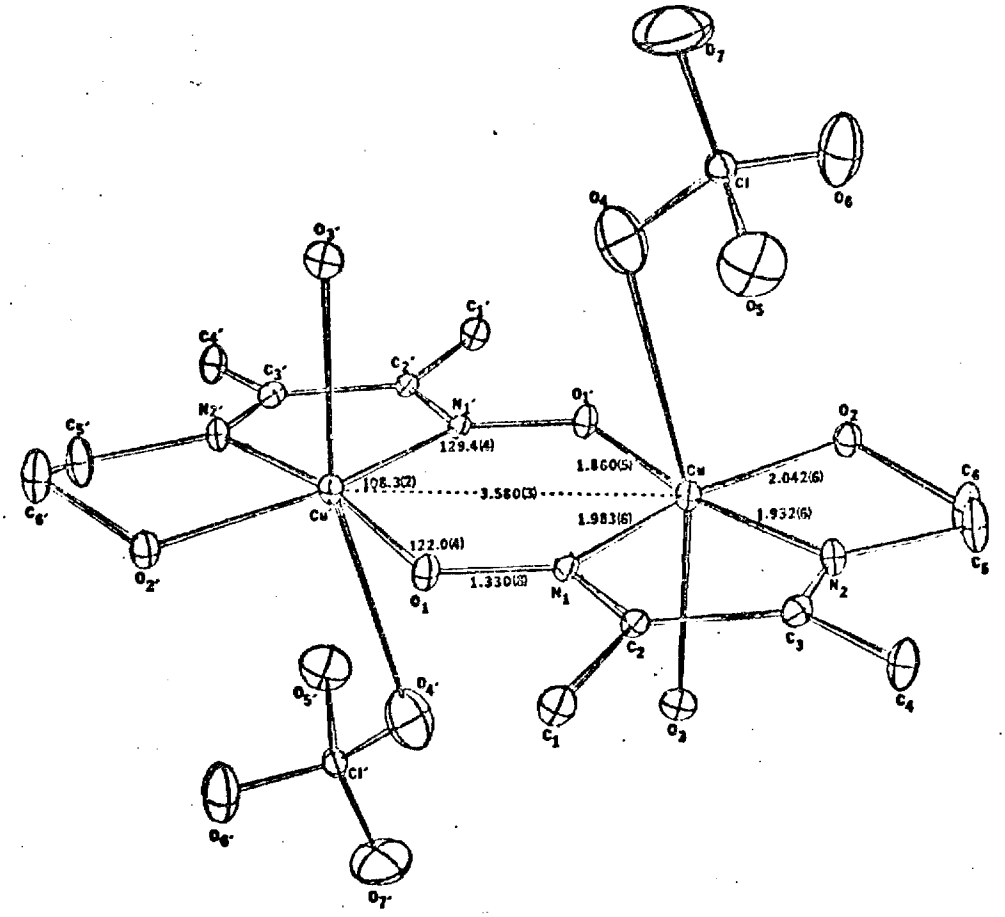


Figure 12

antiferromagnetic coupling but the complex prepared from ethylenediamine (X = NH_2, B = C_2H_4) forms a tetrameric complex with much weaker coupling. The dimeric complex has a planar six-membered ring, $Cu_2O_2N_2$, and the tetrameric complex has two non-planar $Cu_2O_2N_2$ rings and one planar Cu_2O_2 ring. Somewhat different magnetic properties are observed for the copper(II) complexes of other ligands of this type[46] but structure studies

have not been completed. Complexes of these ligands with other metal ions are being studied.

The difference in magnetic properties of these compounds can be explained on the basis of structural features by arguments similar to those used for the four-membered ring compounds. For the low-moment compounds, the planarity of the ring makes a π-system possible but the same problem arises with respect to the location of the unpaired electrons. An explanation similar to that used for the σ-coupling mechanism can be used to explain the stronger coupling in this compound. The symmetry combinations of the two d_{xy} orbitals overlap with very different ligand orbitals, Figure 13, and a larger energy difference would be predicted.

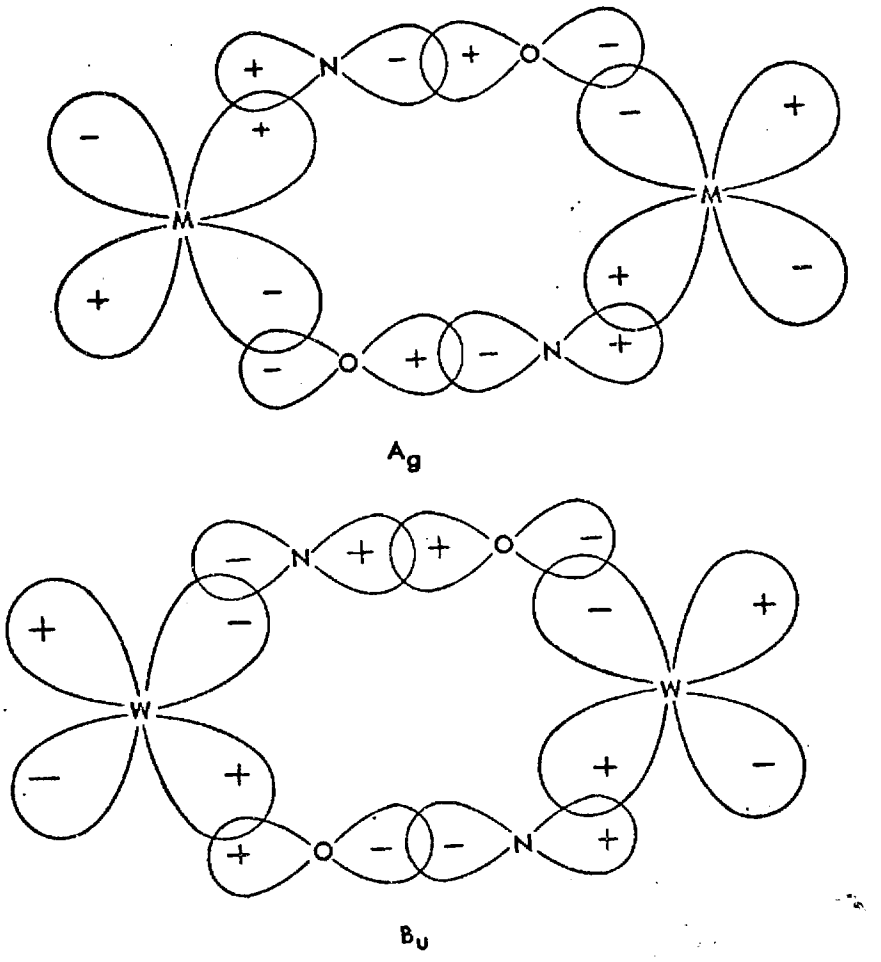


Figure 13

Hydrogen-Bonded Complexes with Aminoalcohols as Ligands.

Although dimer formation through cooperative hydrogen bonding is well documented for compounds such as carboxylic acids, there have been few recognized examples of hydrogen-bonded dimers of transition metal complexes. This type of dimeric complex was first suggested by Yoneda and Kida[47] for a series of compounds prepared from cobalt(III) compounds and 2-aminoethanol. The compounds that they prepared have recently been shown[48-50] to be identical to compounds prepared earlier[2,3] from cobalt(II) salts and 2-aminoethanol. The formula of the compounds, $Co_2(Eta)_3(EtaH)_3X_3$, could be rationalized as a double salt composed of two complex salts, $Co(Eta)(EtaH)_2X_2$ and $Co(Eta)_2(EtaH)X$, but the constant composition for a variety of anions, X, made such an explanation improbable. A hydrogen-bonded cation, $[Co_2(Eta)_3(EtaH)_3]^{3+}$, was suggested and dinuclear structures containing octahedral tris-chelates with from one (corner-to-corner bonding) to three (face-to-face bonding) hydrogen bonds were considered. Similar compounds of chromium(III) have since been reported[51,52] but structure studies have not been reported for any of these compounds. In preparing a series of complexes of various metal ions with tris-(2-aminoethoxido)cobalt(III) as ligands, a compound of composition $[CoNi(Eta)_3(EtaH)_3]I_2$ was isolated.[53] Crystal structure analysis, with an R value of 0.069, has shown a cubic crystal system, Pa3, with dimeric units of $\bar{3}$ symmetry, Figure 14. Two tris chelate complexes, each possessing threefold symmetry, are related by an inversion center. With only four dimers per unit cell, symmetry requires the cobalt and nickel atoms to be disordered over a set of eight-fold positions. Two sets of ligand positions were located and were assumed to correspond to chelate rings on the two different metal ions. The two sets

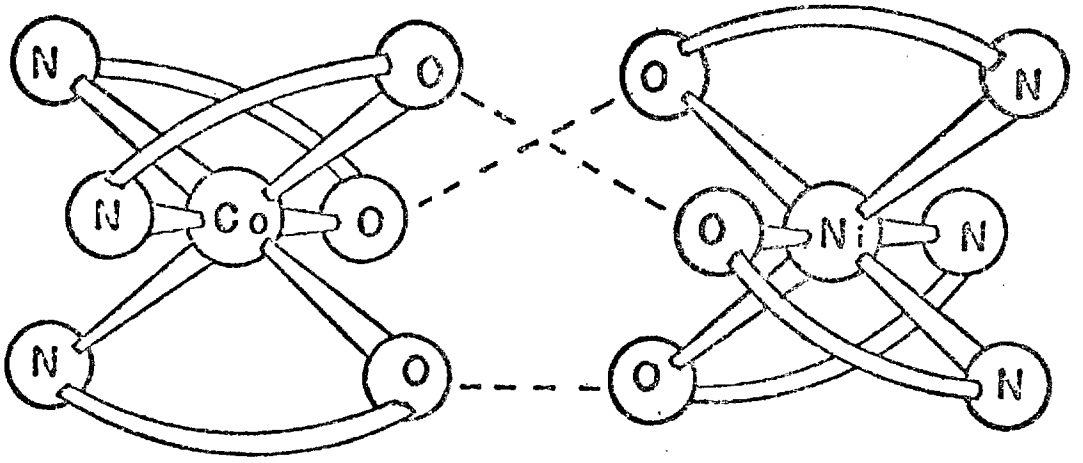


Figure 14

of ligand positions, each with an occupancy factor of 0.5, were used in refining the structure and gave metal-nitrogen and metal-oxygen distances that were reasonable for cobalt(III) and nickel(II) complexes.

Although the disorder makes it impossible to distinguish between a homogeneous structure with cobalt-nickel dinuclear cations and a solid solution made up of a mixture of cobalt-cobalt and nickel-nickel cations, the latter possibility seems less likely due to the different charges on the cations. For a cobalt-nickel dinuclear cation, the oxygen atoms of one tris chelate are 2.51Å from oxygen atoms of the other tris chelate; although hydrogens were not located, the short oxygen-oxygen distance and the stereochemistry at the oxygens are ideal for face-to-face hydrogen bonding.

Compounds with similar formulations have been reported[54] for divalent metal ions cations and a crystal structure analysis[55] for one of these, $Ni_2(Eta)_2(EtaH)_4(ClO_4)_2$, showed it to be isomorphous (space group Pa3, a = 13.85Å) with the cobalt-nickel compound. This structure, which has been refined to an R value of 0.073, also exhibits two-fold disorder of the ligand positions but the occupancy factors refined to values near 1/3 and 2/3 rather

than 1/2. These values indicate four ligands of one type and two of another type for each dimeric unit and lead to two short (2.24Å) oxygen-oxygen distances indicative of edge-to-edge hydrogen bonding. The difference in the two structures can be related to the presence of an additional proton per dimeric unit in this structure; the additional proton would leave only two alkoxide oxygens to participate in hydrogen bonding. The room temperature magnetic moment of the compound, 3.23 B. M. per g. at. of Ni, is a normal value for octahedral nickel(II) and the value at 77°K is only slightly lower, 2.98 B. M. Studies at lower temperatures are needed to determine whether spin-spin coupling occurs through the hydrogen bonds.

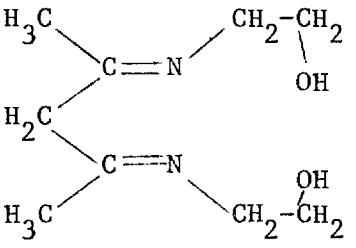
The preparation of an analogous cobalt(II) compound was reported but potentiometric analysis for cobalt(II) and magnetic susceptibility measurements on different preparations indicate a variable cobalt(II)-cobalt(III) ratio, depending on the reaction conditions. The products are isomorphous with the nickel compounds discussed above but a complete structure analysis has not been carried out.

Attempts have been made[55] to prepare a series of related compounds but a cobalt(III)-zinc(II) compound is the only example that has analyzed properly. A complex of copper(II) with the anion of ephedrine, a substituted 2-aminoethanol, was isolated and the structure consists of a triangular arrangement of square-planar copper(II) complexes connected by oxygen-nitrogen-hydrogen bonding.[56] The hydrogen bonding would appear to be rather weak from the N-O distance (2.87Å) but spectral studies and the compound's solubility in nonpolar solvents suggest that the trimers exist in solution as well as in the solid state. The copper-copper distance is 4.07Å and no evidence of magnetic coupling is indicated. Similar interactions in the

structure of $Cu(Eta)(EtaH)(NO_3)$ lead to cyclic tetrameric units and comparison of the magnetic moment at room temperature (1.84 B. M.) with that at 77°K (1.56 B. M.) indicates an antiferromagnetic interaction.

Hydrogen-Bonded Complexes with Iminoalcohols as Ligands

The condensation of two molecules of 2-aminoethanol with one molecule of 2,4-pentanedione leads to a diimine (abbreviated $DiimH_3$), VI, which can



VI

function as a tetradentate ligand. This condensation occurs when 2,4-pentanedione is reacted with various transition metal salts in 2-aminoethanol. When copper(II) or nickel(II) acetate is employed, dark green crystals of empirical formula M(DiimH) are formed.[57] Structure analyses have shown the two compounds to be isomorphous with virtually indistinguishable dimeric species. The dimeric units consist of planar, four-coordinate M(DiimH) units related by an inversion center, Figure 15, and the resulting M-M distance is 4.98Å. Alkoxide oxygens of the two ligands are separated by only 2.30Å and strong hydrogen bonding is suggested. In the refinement of the structure of the copper(II) compound,[58] all hydrogens bonded to carbons were located and a final difference Fourier map (R = 0.046) had its largest peaks at points midway between the oxygen atoms. This result cannot be taken as conclusive evidence of symmetrical hydrogen bonding since disorder of

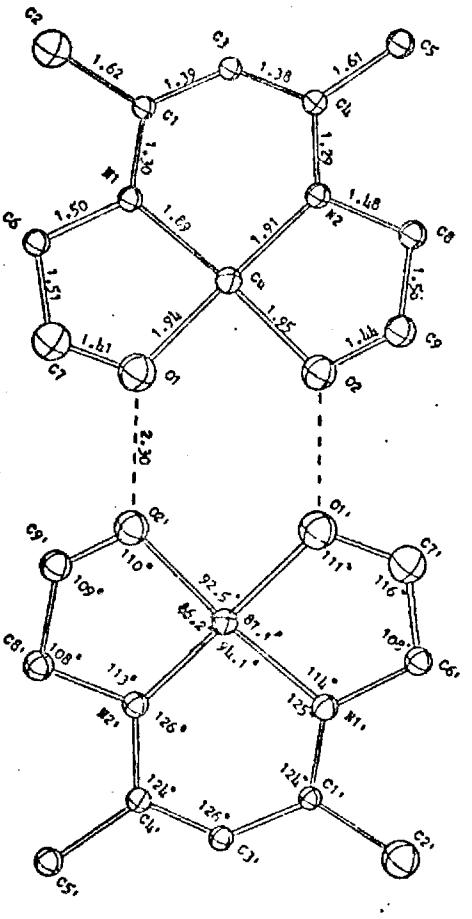


Figure 15

unsymmetrically bonded units could produce the same result.

The hydrogen bonding is cooperative, in the sense of the more familiar carboxylic acid dimers, and this effect no doubt is very important in enhancing the hydrogen bonding. Molecular weight studies show that the dimeric arrangement persists in organic solvents such as chloroform.

There are two independent dimeric species in the unit cell and the two asymmetric units show identical bond distances and bond angles. Although both dimers show edge-to-edge hydrogen bonding, the two units differ in the geometry of the eight-membered ring system. In one unit the metal, oxygen,

and hydrogen atoms of the ring constitute a plane but the other unit shows a definite stepped arrangement with the oxygen and hydrogen atoms in a plane and metal atoms on opposite sides of the plane.

A particularly interesting feature of $[Cu(DiimH)]_2$ is the fact that, despite a metal-metal separation of some 4.979(6)Å, spin coupling occurs between the single unpaired electrons on each copper(II) atom. The room temperature magnetic moment of 1.69 B. M. per gram atom copper is already below the spin only value, 1.73 B. M., and the moment drops to 1.56 B. M. at 193°K and to 1.14 B. M. at 77°K. This behaviour is indicative of antiferromagnetic superexchange with a coupling constant, -2J, of approximately 100 cm^{-1}. Although much larger J-values have been reported for dimeric copper(II) complexes, the value is surprisingly large considering the metal-metal distance and the nature of the bridge. As a means of comparison, hydrated salts rarely exhibit ferromagnetic or antiferromagnetic exchange integrals in excess of 20 cm^{-1}, and thus normal paramagnetic behaviour is usually observed until extremely low temperatures (<20°K) are reached.

Hydrogen-Bonded Complexes with Iminoacids as Ligands

Another series of hydrogen-bonded complexes has been studied. Complexes of a variety of transition metal ions with the imines of salicylaldehyde and amino acids were reported several years ago.[59] From the formulas and magnetic properties reported, several of the complexes appeared to be polynuclear complexes with strong magnetic coupling. From potentiometric determinations of total cobalt and cobalt(II), the unusual magnetic moment of the cobalt compound has been found to result from partial oxidation to cobalt(III). From a diffraction study, the correct formulation is

$[Co(H_2O)_6][Co(Salgly)_2]_2$ (where Salgly represents the dianion of the imine of salicylaldehyde and glycine). The cobalt(II) and cobalt(III) complexes are connected into trimers by hydrogen bonds. Similar compounds are formed by iron and manganese. The presence of iron(II) and iron(III) and the relative amount of each was determined by Mossbauer studies. Although isomorphous with each other, the iron and manganese compounds differ from the cobalt compound in the hydrogen bonding since infinite chains are formed instead of the trimeric units. These complexes are of particular interest because of their relationship to the system used as a model for vitamin B6 reactions[60] and for amine oxidase reactions.[61] Although the salicylaldehyde complexes are not catalysts for these reactions, they are structurally similar to the pyridoxal phosphate complexes which are catalytically active. The structure of a manganese(II) complex of the imine of pyridoxal and valine has been reported previously;[62] however, it has been suggested that the active catalyst contains manganese(III) and some results indicate that both divalent and trivalent metal ions are involved in the reaction.[61] Further studies of the complexes are in progress.

Cubane-type Complexes

Several complexes with cubane-type structures have been prepared and these are of particular interest because of the occurrence of this unit in the ferredoxin structure. A series of compounds with the formula $[M(AA)(CH_3O)(ROH)]_4$ (where M=Co, Ni, or Mg, AA = the anion of a β-dicarbonyl compound, and R = CH_3 or C_2H_5) has been reported[63] and the compounds were found to have the cubane-type structure[64,65] illustrated in Figure 16.

Magnetic studies[66,67] of the nickel compounds of this type have indicated ferromagnetic coupling of the metal ions; a magnetic study of the cobalt compound with AA = acetylacetonate was attempted[68] but partial decomposition made it impossible to obtain good data. The salicylaldehyde and o-hydroxyacetophenone compounds appear to be more stable and magnetic studies of these are in progress.

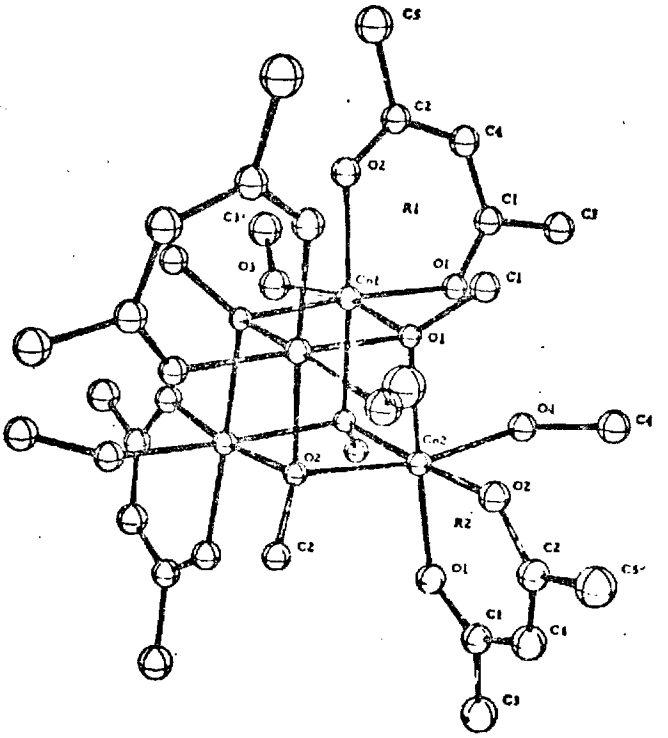


Figure 16

The chemistry of these compounds have been investigated to some extent; studies of alkoxide and alcohol exchange were carried out by refluxing the cubane compounds with various alcohols either in the alcohol or in chloroform. With nickel compounds there was complete exchange of the alcohol, ROH, but no exchange of the methoxide groups; with magnesium compounds, the isolation of $Mg(AA)_2(H_2O)_2$ from the reaction mixtures indicated

decomposition of the cubane units. All of the cubanes of this series for which structure studies have been carried out have had the same arrangement of chelate rings and alcohols even though six geometrical isomers are possible. Preliminary crystallographic data for $[Co(Acac)(CH_3O)(H_2O)]_4$ indicated a site symmetry of $\bar{4}2m$, consistent with only the most symmetric isomer. However, a detailed structure study has revealed disordered molecules of lower symmetry and the same isomeric form as found in the previous studies was obtained by refinement of the data. It is possible that all isomers are present in solution and only the least soluble is being crystallized. Further studies, including NMR studies on solutions of the magnesium cubanes, are being carried out.

The probability of isolating different isomers of inert cobalt(III) complexes led to studies of the oxidation of the cobalt(II) cubane complexes. Although some oxidation was apparent when hydrogen peroxide was added to a solution of the cobalt(II) cubane, the brown crystals that were isolated were paramagnetic. Analyses indicate that the compound is $[Co_4(Acac)_4(CH_3O)_4(C_2H_3O_2)_2]$ and the structure,[69] Figure 17, shows bridging

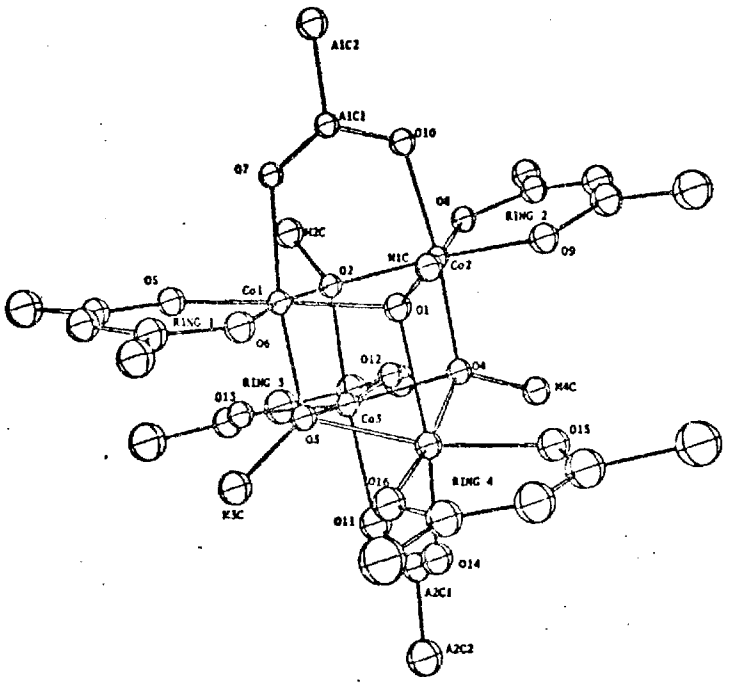


Figure 17

acetates in place of the alcohol groups of the cobalt(II) cubane; the cobalt-oxygen distances are shorter by ca. 0.15Å for one pair of cobalt ions and indicate that these are the cobalt(III) ions. The magnetic moment of 4.98 B. M. per g. at. of cobalt(II) at room temperature decreases slowly with temperature; antiferromagnetic coupling may occur through the acetate bridge but more complete magnetic studies are needed in order to evaluate the magnetic behaviour of this compound. Preliminary results indicate that a similar compound can be prepared in the absence of acetate and further studies are in progress.

Other Oxygen-Bridged Complexes

The 1:1 adducts of cobalt(II) and nickel(II) acetylacetonates with cyclohexylamine, illustrated in Figure 18, have been shown to be dimeric and to have planar four-membered rings consisting of metal ions and acetylacetonate

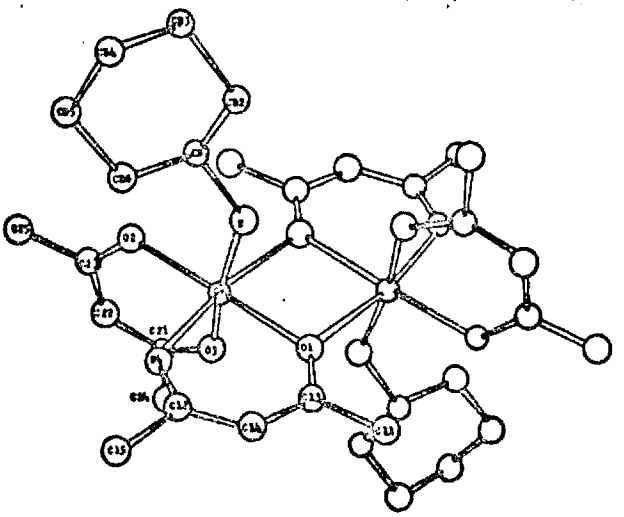


Figure 18

oxygens;[70] although the room temperature magnetic moments are normal spin-

coupling may only be effective at lower temperatures and magnetic studies at lower temperatures are being carried out. More recently, 1:1 complexes of these metal acetylacetonates and pyridine N-oxide have been prepared in our laboratories; the cobalt(II) and nickel(II) compounds gave identical powder patterns and a structure determination shows pyridine oxide bridging groups.

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